Heats of Dilution and their Variations with Temperature

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BY

FRANK R. PRATT

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HEATS OF DILUTION AND THEIR VARIATIONS WITH TEMPERATURE.*

BY

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1. *Enunciation of the Purpose of the Investigation.*—By thermodynamic calculations the variation of the heat of dilution of a solution with change of temperature is equal to the rate at which the heat capacity of the solution changes with the concentration. Previous determinations of the heats of dilution have failed to support this relation in some cases.[1] It is the object of this research to find out, if possible, whether this discrepancy is real or the result of experimental error.

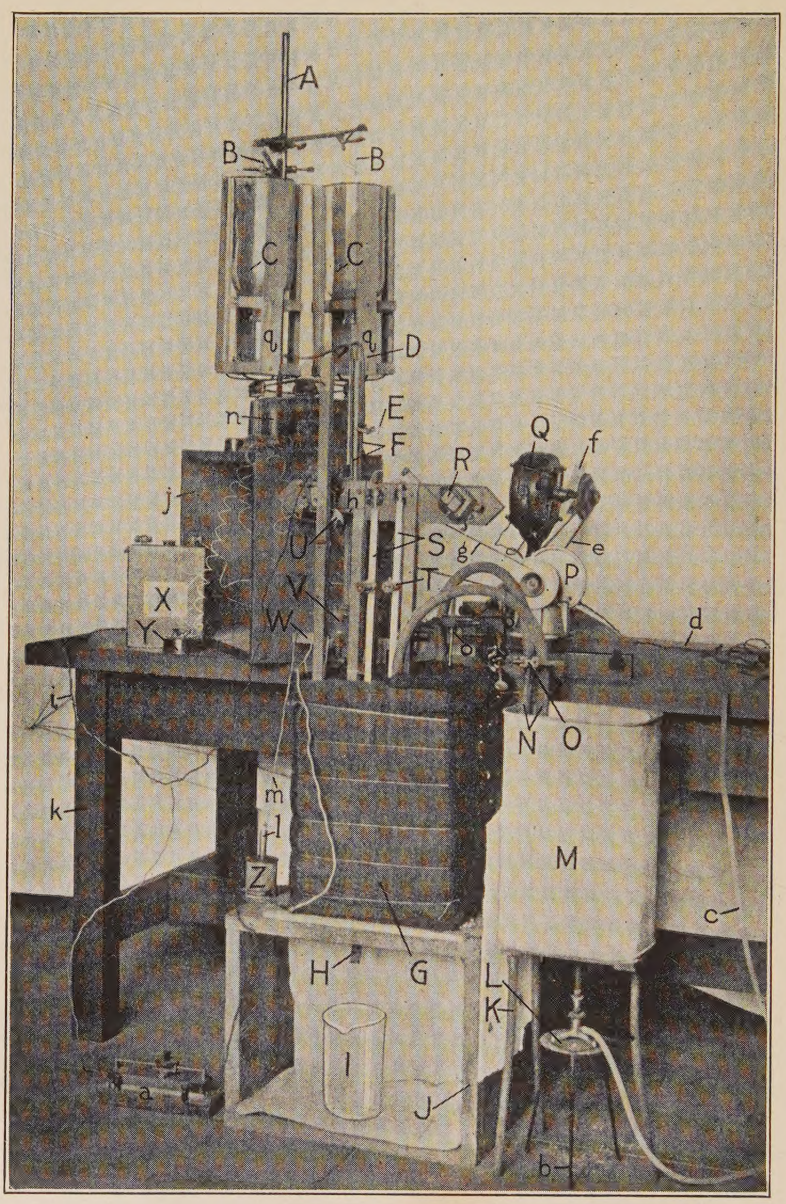
2. *Method of Obtaining Heats of Dilution.*—In determining the heats of dilution it is necessary to start with an initial concentration of the solution and measure the amounts of heat L_m evolved as the solution is diluted by adding to it mass m of water. The values of L thus obtained plotted against the values of m give a curve whose tangent at any point is the value of the heat of dilution for the corresponding concentration.

3. *Problem of Apparatus.*—Magie's experiments on heats of dilution were performed with silver calorimeters exposed to room temperature. On account of continual temperature change when the readings were taken it was necessary to make corrections, and these were somewhat uncertain. The problem was to devise a piece of apparatus that would measure the heat of dilution as accurately as possible. At the suggestion of Prof. H. L. Cooke, I decided to employ a method of continuous flow. In designing the several parts of the apparatus I was greatly assisted by Professor Cooke's experience and advice. The apparatus was planned so that either mercurial or platinum resistance thermometers could be used. After a thorough consideration of resistance thermometers they were abandoned in favor of mercurial thermometers, because the latter simplified the manipulation of the apparatus so that one person could use it.

* Communicated by the Author.

[1] Magie, "Heats of Dilution," *Physical Review*, vol. xxxv, October, 1912.

FIG. 1.



4. *Description of Apparatus.*—The principal parts of the apparatus were a delivery system by which equal masses of water and solution flowed continuously through the apparatus, and a thermostatic system by which the water and solution in separate tubes were brought to the same temperature, then mixed in a Dewar flask and the change in the temperature of the mixture noted. The complete arrangement of these systems is shown in Fig. 1, in which the several parts are marked with letters. Each part has the same letter in all the diagrams.

The delivery system consisted of two glass tanks, *C*, in which the liquids to be used were contained. These tanks were supported upon the pans of a balance, *n*, and the liquids were conducted from the tanks to the thermostatic system through rubber tubes which were supported at a point in line with the centre knife-edge to preserve the sensitiveness of the balance.

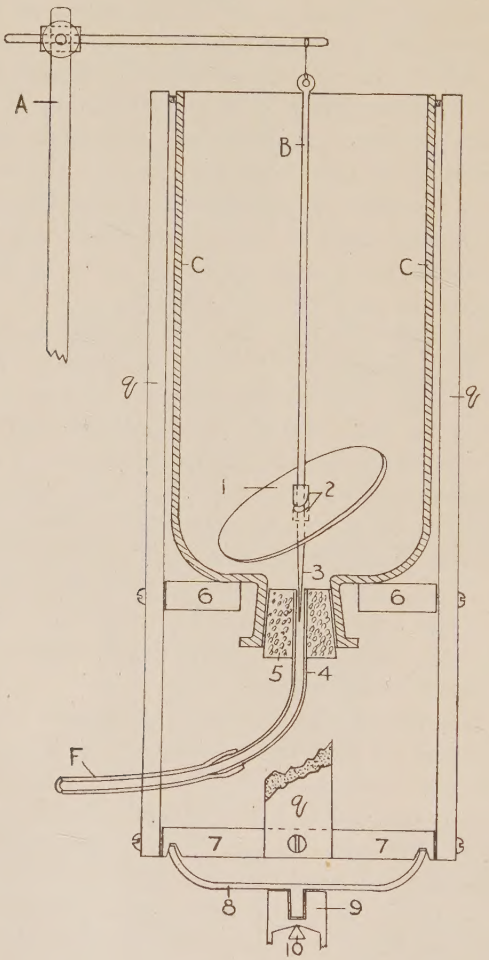
The device for controlling the flow of the liquids was the same in both tanks, hence the detailed diagram given in Fig. 2 shows only the right half of the delivery system. The stand, *A*, supports a small glass rod, *B*, on the lower end of which is a long conical valve, 3, which controls the rate of flow of the liquid. Valve 3 remains stationary while the tank moves up or down, thus decreasing or increasing the area of the opening through which the liquid leaves the tank. The tank having the greater mass of liquid will move down, opening its valve, and at the same time the other tank having less mass will move up and partly close its valve, thus automatically keeping the masses of liquids in the two tanks equal.

A test of this device showed that the balance oscillated continuously. Instead of two equal streams, there was a jet first from one tube and then from the other. A thin glass disc, 1, fastened to rod *B* in a horizontal position, decreased the number of vibrations, but did not overcome the difficulty. But by tilting the disc the least movement of the liquid up or down forced valve 3 against the side of the outlet tube, 4, causing friction which arrested the balance before it swung too far, and so the desired continuous flow was attained.

A detailed diagram of the thermostatic system is shown in Fig. 3. The several parts of this system were placed in a rectangular tank, 18, which was insulated with felt, 19, and filled with water. Two silver tubes, 9, received the liquids from

the delivery system and carried them to the mixing tube, 2, of the Dewar flask, 1. Each of these silver tubes was 2 millimetres in diameter and 3.8 metres long. This length of tubes gave the liquids which they conveyed abundant opportunity to acquire

FIG. 2.



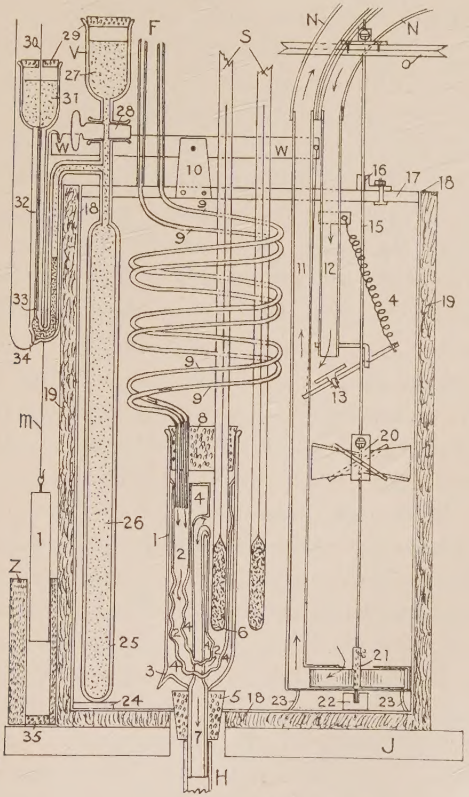
the constant temperature of the water in which the tubes were immersed. A vigorous circulation of the water was maintained by the revolving stirrer, 20.

The mixing tube was corrugated to aid in mixing the liquids, and was insulated by vacuum to prevent transfer of heat. Ar-

rows show the course of the mixture flowing around the thermometer bulb, 6, and out through the overflow tube, 7. The other thermometer, *S*, indicates the temperature of the water in the thermostat.

The temperature of the thermostat was maintained at the desired point by means of a circulatory system, which consisted

FIG. 3.



of a centrifugal pump, 21 (Fig. 3); an outlet tube, 11; a copper coil in the tank, *M* (Fig. 1); a return tube, 12 (Fig. 3); and a control valve, 13. The centrifugal pump forced a small amount of water from the thermostat through the system and back to the thermostat again. The copper coil was surrounded with ice or immersed in hot water, according as the desired temperature of the water in the thermostat was below or above 20° C.

In order that the right amount of cold or hot water might be delivered to the thermostat to maintain constant temperature, a sensitive control system was constructed. This system consisted of a long tube, 25 (Fig. 3), filled with toluene; a capillary U-tube, 32, containing mercury for closing an electric circuit which operated a solenoid, *Z*; and a control valve, 13, which was opened or closed by a solenoid plunger, *l*, acting through lever, *W*.

When the stopcock, 28, is closed the expansion of the toluene forces the mercury, 33, up to meet a wire, 30. This unites the wires 30 and 34 which are connected in series with a solenoid, *Z*. Wire 30 is pushed down by a cam, *U* (Fig. 1), at a constant rate until the push-rod holding the wire slips off the large part of the cam, breaks the circuit at the cam, and quickly pulls the wire out of the mercury. This operation was repeated every ten seconds. The advantages of this moving wire were the prevention of sparking between the mercury and the wire and the stopping of the flow of hot or cold water into the thermostat at short intervals so that the lag in the controller would not allow too much water to enter. Alcohol, 31 (Fig. 3), kept the surface of wire 30 clean. A pinchcock, *O* (Fig. 1), served for the rough adjustment of the flow through the circulatory system. With a careful adjustment of the pinchcock *O*, the temperature would not vary 0.001° for a period of five minutes while readings were taken. When the liquids ceased to flow the temperature would change two- or three-hundredths of a degree before the controller acted. There would be a similar amount of change in the opposite direction when the liquids began to flow.

5 *Tests of Correct Working of Apparatus.*—At first each silver tube in the thermostatic system was only 1.9 metres long. Tests were made by running water through these tubes separately and jointly to determine if the temperature of the water as it left the tubes was constant under all conditions when the temperature of the thermostat was kept constant. These tests showed that a change of five degrees in the temperature of the water as it entered these tubes produced a change of five-thousandths of a degree in the temperature of the water leaving the tubes. To prevent this change of temperature the length of these silver tubes was doubled. After this was done the temperature of the water leaving the tubes remained the same even with a change of

twenty degrees in the temperature of the water as it entered the tubes.

A strong solution of common salt was run through each tube separately and then through both at once, with the result that the thermometer always registered the same as when distilled water was used. Usually the thermometer in the Dewar flask registered four- or five-thousandths of a degree higher than the thermometer in the thermostat. This, no doubt, was due to the vigorous stirring in the mixing tube. If the thermometer in the thermostat stood at 15.000° C., the thermometer in the Dewar flask always registered 15.004° C. when water or salt solution alone flowed through the apparatus.

When distilled water flowed through one tube and an equal mass of salt solution flowed through the other (the thermometer in the thermostat still standing at 15°), the thermometer in the Dewar flask changed from 15.004° C. to some other temperature —for example, to 14.754° C.—owing to the heat of dilution, and continued to register this temperature until the tanks of the delivery system were empty. This zero method allowed the 0.250° C. change of temperature to be measured by the thermometer in the Dewar flask alone, hence no correction for slight differences in the two thermometers was needed.

The contents of the Dewar flask were only a few thousandths of a degree lower in temperature than the surrounding thermostat, hence no radiation correction was necessary. When the flow of liquids stopped, the thermometer in the mixing tube continued to register the same temperature for some minutes, showing good insulation. Even the heat arising from the friction of the liquids running through the mixing tube was compensated by the zero method. Electric hammers were arranged to tap both thermometers before each reading was taken, magnifying glasses fastened to each thermometer aided materially in estimating to thousandths of a degree, and the fact that both thermometers remained constant for several minutes while readings were taken inspired great confidence in the correctness of the readings.

6. *Method of Taking Measurements.*—In cases when the solubility permitted, the initial solution consisted of 25 gramme-molecules of water to one gramme-molecule of salt. The initial concentration, on the convention that $c = 10000/N$, is therefore 400. By running this solution through the apparatus and an equal

mass of water the concentration is changed to 188 in the case of sodium chloride and to different values for other salts. In order to have uniformity in tabulating measurements, the change in temperature resulting from this first dilution was placed in a column marked 1. When this solution was diluted a second time by adding again a mass of water equal to the mass of the solution, the change of temperature was placed under the heading marked ½, the third dilution under ¼, etc. This process was continued until the solution was so dilute that no change of temperature could be detected.

There was no advantage in repeating the measurements at the same temperature, because the results were always the same. But since there is a continuous change in the heat of dilution as the initial temperature is varied, it was of advantage to make a large numbers of measurements with a small increase of temperature in each successive measurement. A variation of two degrees for the chlorides and of five degrees for the other solutions was used. The change in temperature resulting from dilution was plotted against the initial temperature of the solution and water before mixing and a smooth curve passed through these points. This method tended to eliminate small errors in the thermometer by using a different part of the scale of the thermometer each time. It also compensated for the personal factor, since a different number was estimated each time.

7. *Method of Computing Heats of Dilution.*—As the method of calculation was the same for all solutions, a full explanation for any one of them, *e.g.*, sodium chloride, is sufficient. The concentrations for the several dilutions of the sodium chloride solution were calculated and found to be 400, 188, 91.1, 44.9, and 22.3. The heat capacities corresponding to these concentrations were interpolated from tables given by W. F. Magie, *Physical Review*, vol. xxv, No. 3, and were found to be 448.2, 949.5, 1864, 3994.3, and 8043.8, respectively. The heat capacity multiplied by the change of temperature gives the number of gramme-calories of heat which must be introduced into the solution or withdrawn from it to keep the temperature constant.

To compute the heat of dilution of sodium chloride at 10° C., the point is found at which curve 1 (Plate A) cuts the 10° line. This is at −0.297°. This number, multiplied by the heat capacity 949.5, gives −282 calories, which is the value of L for concen-

PLATE A.

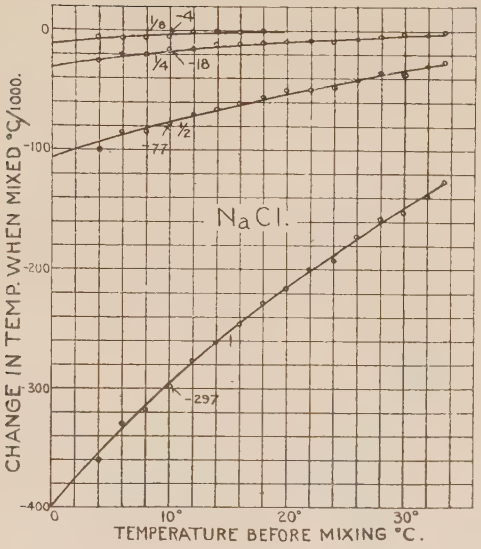
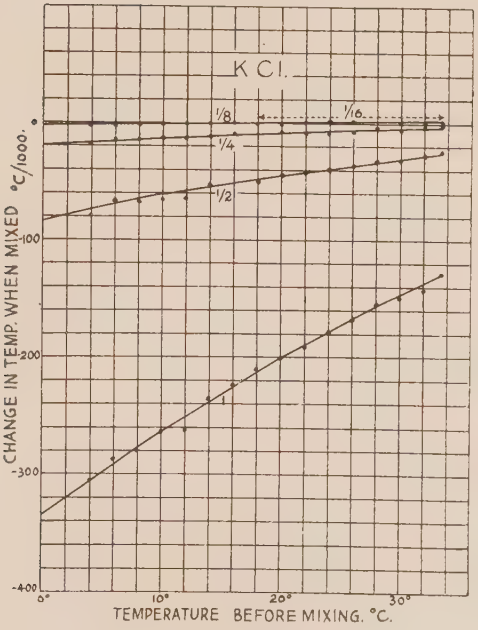
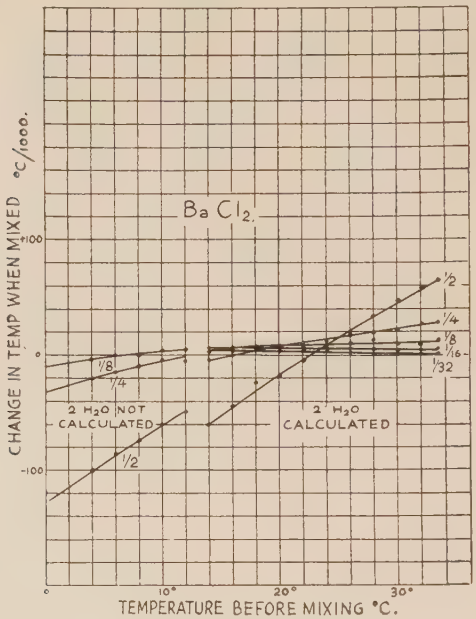


PLATE B.



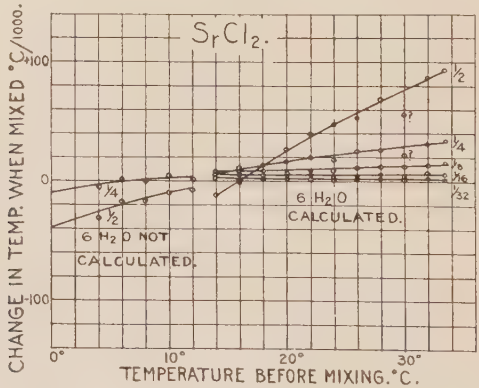
tration 188. Curve ½ cuts the 10° line at −0.077°, and this number, multiplied by 1964 and added to −282, equals −433

PLATE C.



calories, which is the value of L for concentration 91.1. Curve ¼ cuts at −0.018°. This number, multiplied by 3994.3 and

PLATE D.

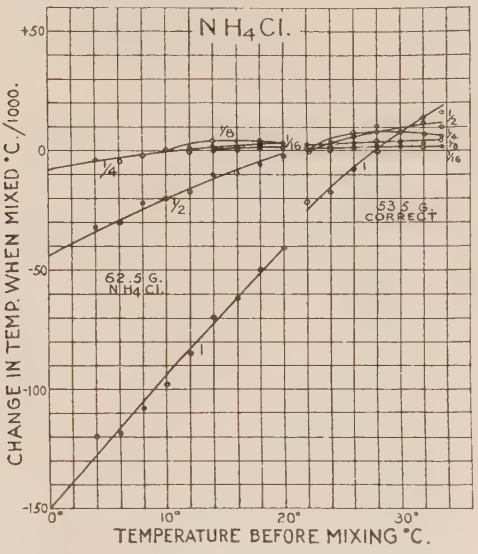


added to −433, gives −505 calories. Finally, curve ⅛ cuts at −0.004°, which, multliplied by 8043.8 and added to −505, gives

−537 calories. These values of L were plotted against the corresponding concentrations and the several points connected by a smooth curve which gave the curve marked 10° in Plate F. This same process was followed in determining the curves for other temperatures.

In part of the measurements for barium and strontium chloride the water of crystallization was not allowed for. At temperatures below 20° by mistake nine grammes too much ammonium chloride was used. It was supposed to be possible to interpolate the correct values from these results until it was too late to

PLATE F.



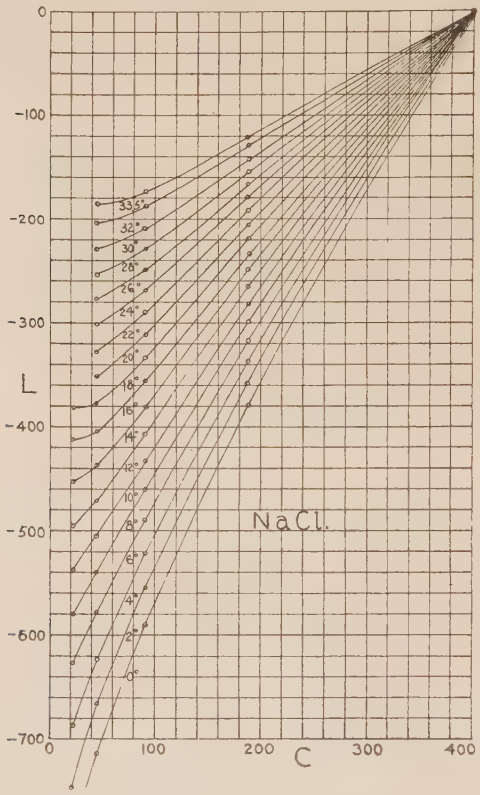
repeat the measurements. The curves are similar to the correct curves, but slightly displaced. It was thought worth while to give these curves, as they show the effect of changing the initial concentration.

Sodium and potassium hydroxide have great affinity for water. As it was impossible to determine the weight of water in the samples used, a solution of each was made and the concentration was determined by finding the density of the solution. The first solution contained 13.5 gramme-molecules of water to one gramme-molecule of sodium hydroxide. The second solution contained 15.2 gramme-molecules of water to one gramme-mole-

cule of potassium hydroxide. These concentrations were about double the initial concentration used in sodium chloride, hence the first curve is marked *2*.

Barium nitrate dissolves slightly in water; thus one-eighth of a gramme-molecule of this salt was dissolved in 25 gramme-molecules of water for the initial solution.

PLATE F.



8. *Statement of Relations to be Examined.*—The formula to be tested is

$$\frac{dl}{d\theta} = -\frac{dH}{dm} \quad \text{(a)}$$

in which l stands for the heat of dilution and is positive when heat has to be removed to keep the temperature θ constant as dilution proceeds. H is the heat capacity of the system, consist-

PLATE G.

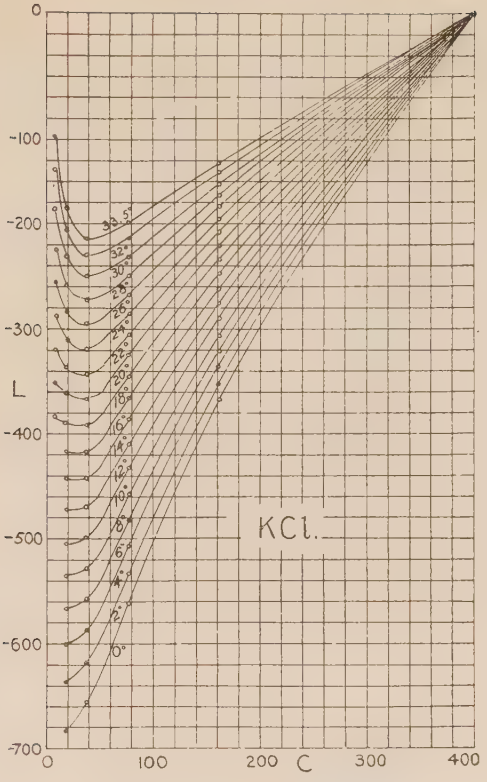
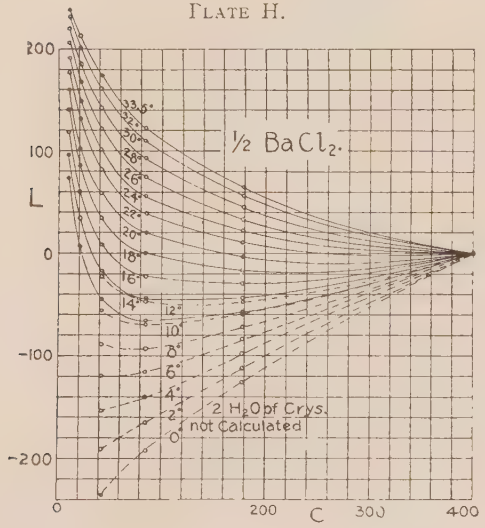


PLATE H.



ing of one gramme-molecule of a salt dissolved in N gramme-molecules of water and an additional mass of water. m is the mass of the solution. Magie has assumed $\frac{dH}{dm}$ to be constant

PLATE I.

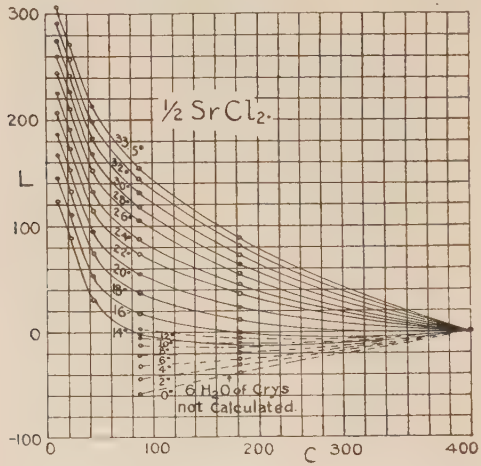
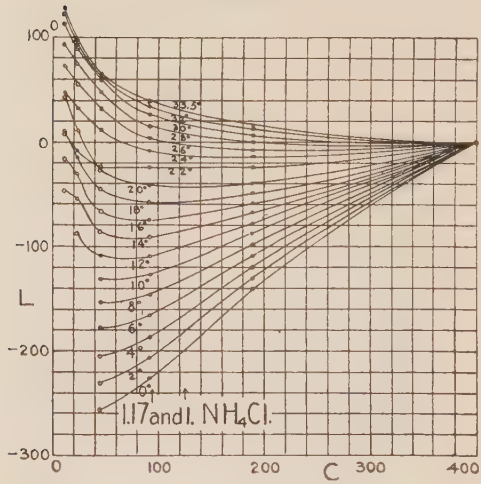


PLATE J.



with respect to temperature.[2] This allows formula (a) to be integrated into the form

$$l_2 - l_1 = -a(\theta_2 - \theta_1) \quad \ldots\ldots\ldots\

PLATE K.

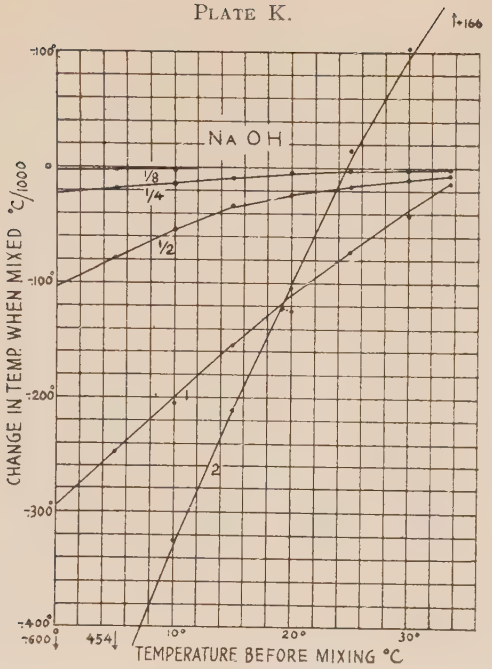
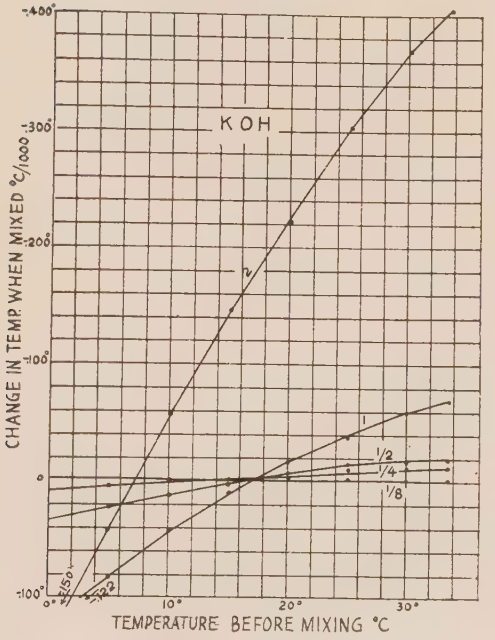


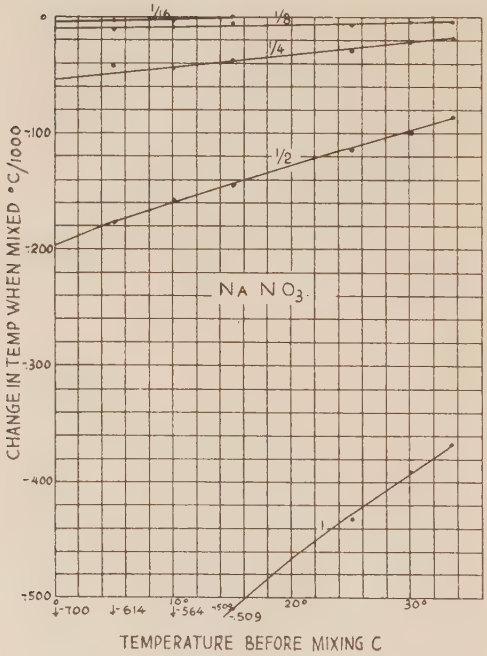
PLATE L.



Since the heat of dilution is obtained by starting with an initial concentration of the solution and measuring the amount of heat L_m evolved as the solution is diluted by adding to it mass m of water, equation (b) may be written in the form:

$$\frac{dL}{dm_2} - \frac{dL}{dm_1} = -\frac{dH}{dm}(\theta_2 - \theta_1) \quad \ldots\ldots\ldots\ldots\ldots\ldots (c)$$

PLATE M.



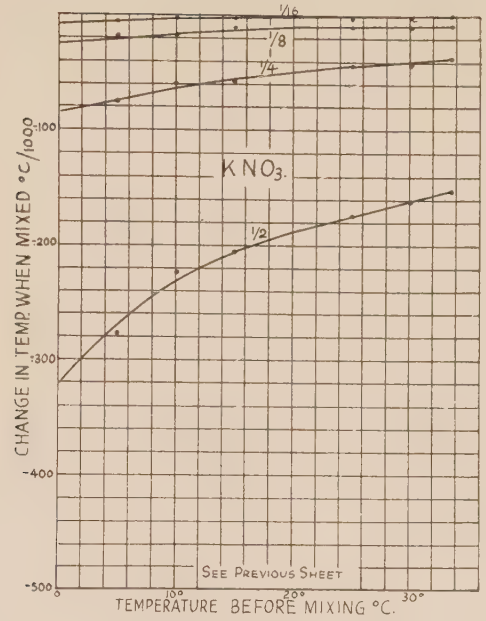
This expression integrated with respect to mass and the temperature assumed to be constant gives

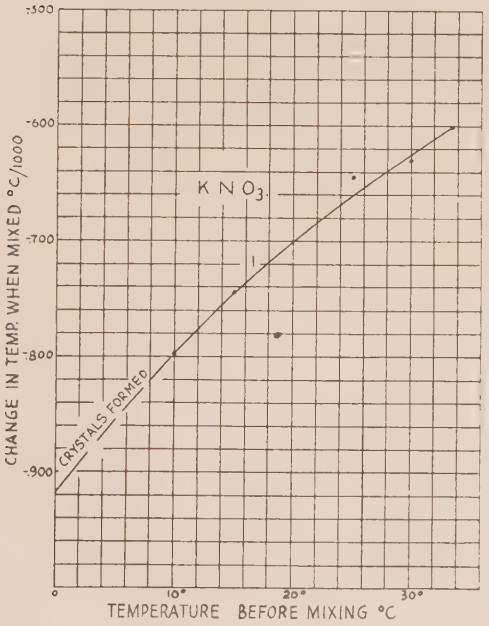
$$(L_m - L_o)_2 - (L_m - L_o)_1 = -(H_m - H_o)(\theta_2 - \theta_1) \quad \ldots\ldots\ldots\ldots\ldots\ldots (d)$$

where subscripts m and o refer to final and initial concentrations. Since L_o equals 0, formula (d) may be written in the form

$$\frac{L_2 - L_1}{\theta_2 - \theta_1} = -(H_m - H_o) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (e)$$

PLATE N.


1/16
1/8
1/4
KNO3.
1/2
CHANGE IN TEMP. WHEN MIXED °C/1000
-100
-200
-300
-400
-500
SEE PREVIOUS SHEET
0
10°
20°
30°
TEMPERATURE BEFORE MIXING °C.


-500
-600
-700
-800
-900
KNO3.
1
CRYSTALS FORMED
CHANGE IN TEMP. WHEN MIXED °C/1000
0
10°
20°
30°
TEMPERATURE BEFORE MIXING °C

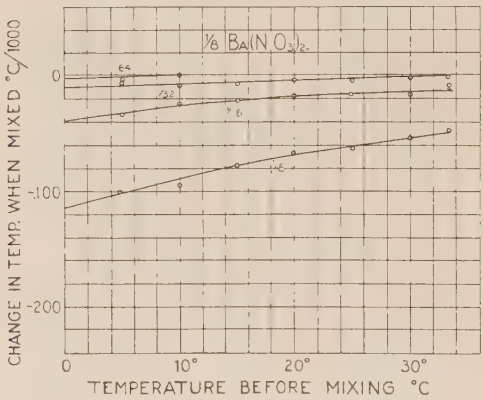
The following tables show the values of equation (e) for the several solutions tested:

Tables for Values of $\frac{L_2 - L_1}{\theta_2 - \theta_1}$ and $-(H_2-H_1)$.

NaCl. $H = 448.2$

θ_2-θ_1	200	100	50
10–4	8.5	14.0	19.2
20–10	7.0	11.8	14.9
30–20	5.7	9.8	12.1
$-(H_2-H_1)$	6.0	10.2	13.8

PLATE O.



KCl. $H = 440.3$

θ_2-θ_1	200	100	50	25
10–4	6.4	10.5	14	15.7
20–10	5.4	9.7	12.5	14
30–20	4.6	7.2	11.9	12.2
$-(H_2-H_1)$	8.3	13.1	18.1	22.2

$\frac{1}{2}$ $BaCl_2$. $H = 430.6$

θ_2-θ_1	200	100	50	25
24–14	6	9.7	12.2	13
33.5–25	5.2	8.2	9.7	8.9
$-(H_2-H_1)$	6.2	10	13.7	16.6

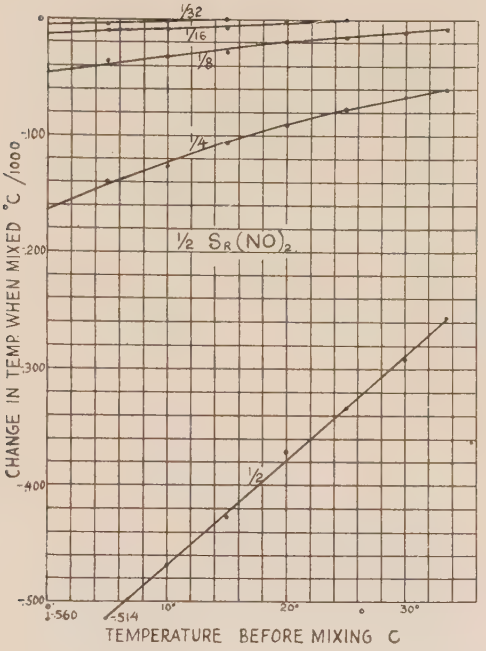
$\frac{1}{2}$ $SrCl_2$. $H = 430$

θ_2-θ_1	200	100	50
24–14	5.2	8.5	9.8
33.5–24	4.2	6.6	8.1
$-(H_2-H_1)$	6	10.4	15.1

NH₄Cl. $H = 445$

θ_2-θ_1	200	100	50
33.5–22	3.3	5.7	5.6
$-(H_2-H_1)$	2	4	6

PLATE P.



NaOH. (1.847) $H = 441$

θ_2-θ_1	400	200	100	50
10–5	11.6	20.4	31.0	37.4
20–10	9.8	19.3	25.4	32.1
30–20	7.8	16.6	19.6	22.6
$-(H_2-H_1)$	5.88	10.88	15.88	18.88

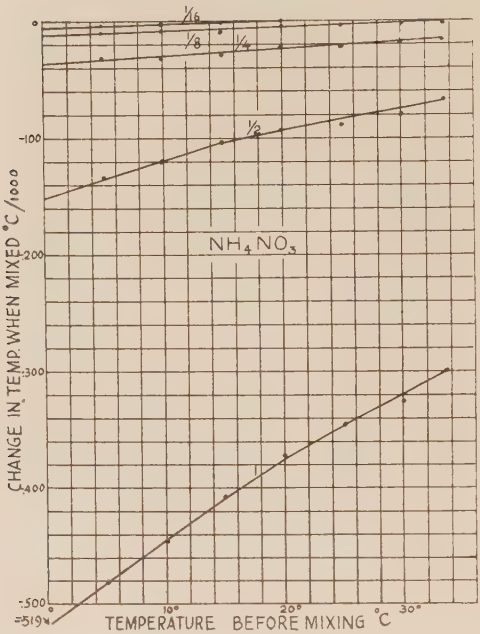
KOH. (1.645) $H = 421$

θ_2-θ_1	400	200	100	50
10–5	7.2	17	24.2	28.4
20–10	6.8	14.4	20.2	24.3
30–20	5.5	11.3	16.7	19.2
$-(H_2-H_1)$	9.4	16.4	22.4	26.4

$NaNO_3$ $H = 467$

$\theta_2-\theta_1$	200	100	50	25
10–5	11.2	16	20.8	22.8
20–10	8.4	15.2	21.3	22.2
30–20	6.8	13.6	18.8	19.4
$-(H_2-H_1)$	8.8	14.5	19.0	23.4

PLATE Q.



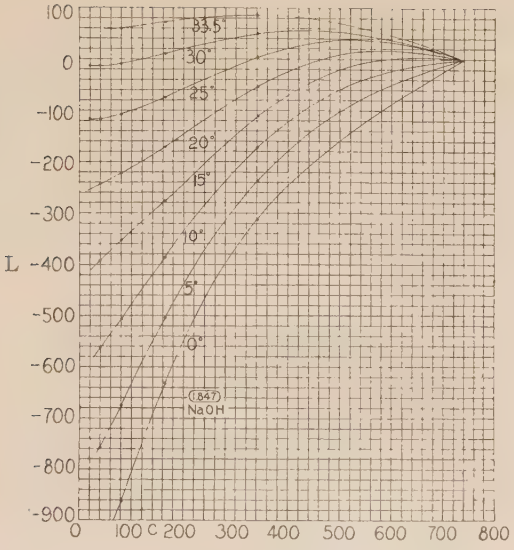
KNO_3. $H = 462$

$\theta_2-\theta_1$	200	100	50	25
10–5	10.4	24	35.2	45.2
20–10	8.8	17.2	23.8	27.4
30–20	6.8	12	16.2	17.8
$-(H_2-H_1)$	9.9	18.6	25.2	31.2

$\frac{1}{8}$ $Ba(NO_3)_2$. $H = 448.9$

$\theta_2-\theta_1$	200	100	50	
10–5	2	4.2	6.8	
20–10	2	3.5	5.2	
30–20	1.3	2.1	3.2	
$-(H_2-H_1)$	1.8	3.9	For $\frac{1}{2}$ $Ba(NO_3)_2$	

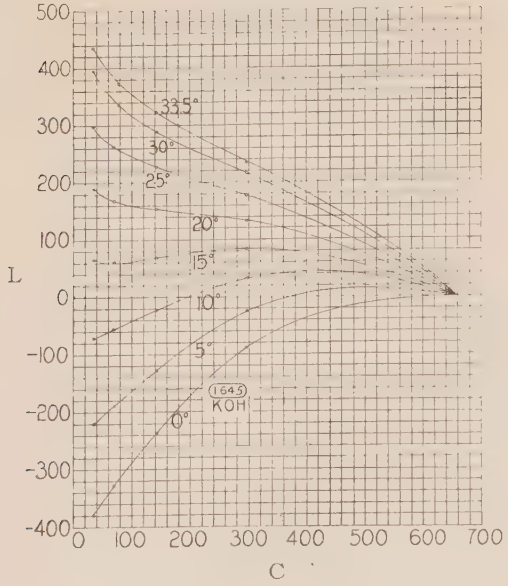
PLATE R.



½ $Sr(NO_3)_2$. $H = 452.7$

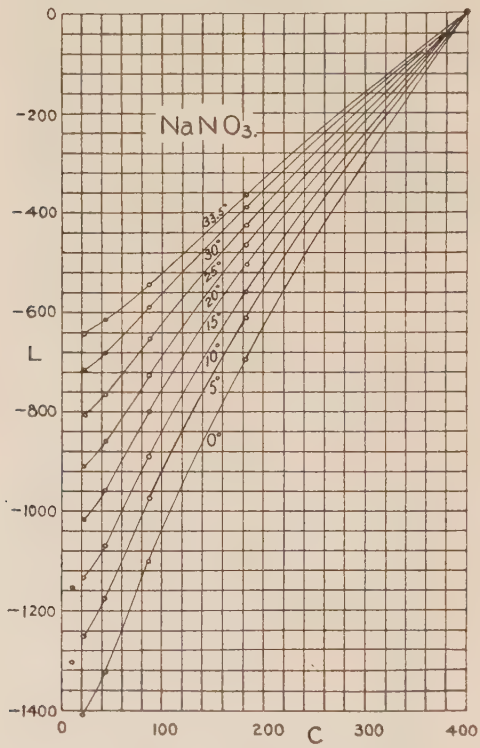
θ_2-θ_1	200	100	50
10–5	8.4	16.4	20.8
20–10	7.6	14.4	19.2
30–20	7.8	12.4	17.2
$-(H_2-H_1)$	7.7	11.7	15.0

PLATE S.



9. *Discussion of Results of Tests of Formula.*—In a general way the formula seems to hold. The values of $-(H_2-H_1)$ in KCl and $SrCl_2$ are too large, and in NaOH they are too small. The initial solution used to obtain the (L, C) curve contained 1.847 gramme-molecules of NaOH, while only one gramme-molecule was used to obtain the value for $-(H_2-H_1)$. This difference accounts for the lack of agreement in the NaOH solu-

PLATE T.



tion, but there is no known reason for the lack of agreement in the other two.

The value of $\frac{L_2-L_1}{\theta_2-\theta_1}$ in every solution decreases considerably with increase of temperature. This fact contradicts the assumption that dH/dm is a constant. The single value of $-(H_2-H_1)$ for each concentration assumes that the value does not change with the temperature. There must be a change, however, if equation (e) holds for all temperatures. Since equation (e)

was found by assuming that dH/dm was constant, it is necessary to modify equation (e). It is a well-known fact that the specific heat of water decreases a small amount between 0° and 33°, and, since a large part of the system is water, the heat capacity

PLATE U.

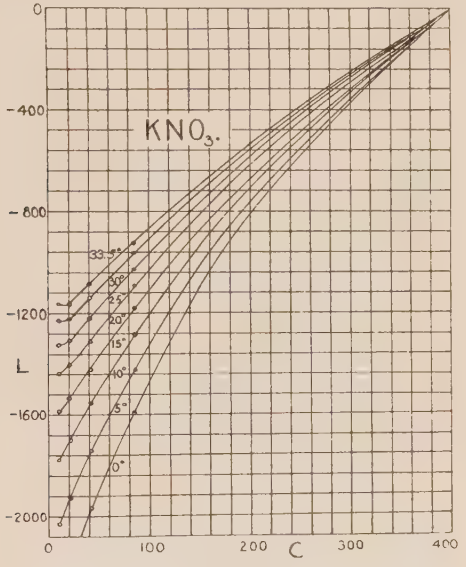
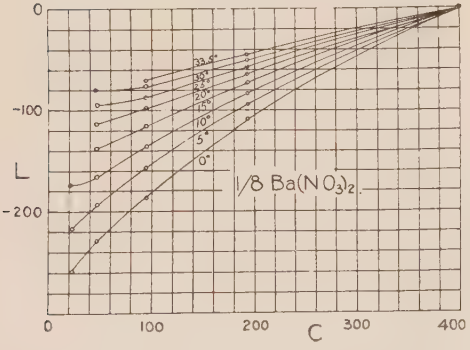


PLATE V.

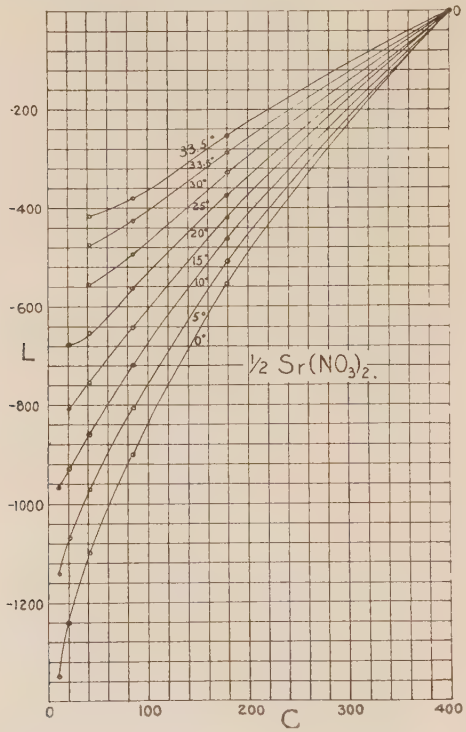


must change with the temperature. Teudt has shown that the change in the heat capacity of a salt solution with change of temperature is in general less than that of water.[3]

[3] Inaug. Diss. Erlangen, *Beiblatter*, xxiv, p. 1104 (1900).

The specific heats of the several salts increase with increase of temperature, hence, if the properties of a concentrated solution are additive, we may assume the specific heat of the solution to be constant, or more nearly so than water. As there is no very definite knowledge on this point, suppose we assume the specific heat of a concentrated salt solution to be constant.

PLATE W.



10. *Modification of Relations.*—When the heat capacity of the solution is assumed to be constant with respect to the temperature it is possible to derive relations which more nearly fit the experimental values. Let

M = the total mass of water in the system.
m = the mass of water in the solution.
$M-m$ = the mass of water outside of the solution.
h = the heat capacity of the solution.
S = the specific heat of the solution.
σ = the specific heat of the water outside of the solution.

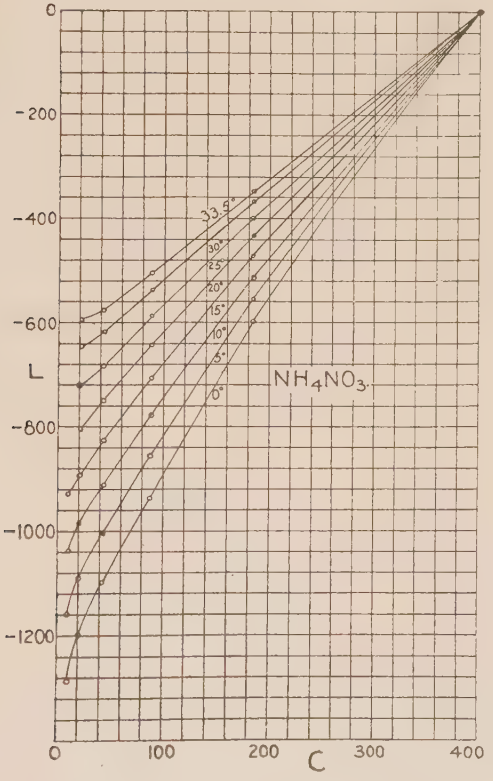
Then $H_o = Sm + \sigma\,(M - n)$. A small mass of water, dm, transferred from the supply outside of the solution, to the solution gives the heat capacity

$$H_1 = (S + \frac{dS}{dm}\,dm)\,(m + dm) + \sigma\,(M - m - dm)$$

and

$$H_1 - H_o = Sdm - \sigma\,dm + m\frac{ds}{dm}dm$$

PLATE X.



but

$$H_1 - H_o = dH$$

therefore

$$\frac{dH}{dm} = S - \sigma + m\frac{dS}{dm} \qquad \text{(f)}$$

$h = mS$ and $dh = mdS + Sdm$

therefore

$$\frac{dh}{dm} = m\,\frac{dS}{dm} + S$$

This equation, substituted in (f), gives

$$\frac{dH}{dm} = \frac{dh}{dm} - \sigma$$

This value of $\frac{dH}{dm}$, substituted in (a), gives

$$\frac{dl}{d\theta} = -\left(\frac{dh}{dm} - \sigma\right) \quad \text{(g)}$$

By integration

$$l = -\left(\frac{dh}{dm}\right)\theta + \int \sigma\, d\theta + e$$

When this equation is integrated with respect to m, and θ is constant, we obtain

$$L_1 - L_o = -(h_1 h_o) \cdot - (\theta_1) + \int\int \sigma\, d\theta\, dm + e dm \quad \text{(h)}$$

or

$$= -(h_1 - h_o)\,(\theta_1) + (M_1 - M_o) \int \sigma d\theta + e dm$$

and

$$L_2 - L_o = (h_1 - h_o)\,(\theta_2) + (M_1 - M_o) \int \sigma d\theta + e dm \quad \text{(i)}$$

When (h) is subtracted from (i),

$$L_2 - L_1 = (h_1 - h_o)\,(\theta_2 - \theta_1) + (M_1 - M_o) \int_{\theta_1}^{\theta_2} \sigma\, d\theta \quad \text{(j)}$$

Equation (j), divided by $\theta_2 - \theta_1$, gives

$$\frac{L_2 - L_1}{\theta_2 - \theta_1} = (h_1 - h_0) + \frac{M_1 - M_0}{\theta_2 - \theta_1} \int_{\theta_1}^{\theta_2} \sigma d\theta \quad \text{(k)}$$

The left sides of equation (k) and (e) are equal. The right side of equation (k) shows the variation of $-(H_2 - H_1)$ which must be used in the cases tested, when the change in the specific heat of water with respect to the temperature is taken into account.

The formula for the specific heat of water proposed by Callendar[4] for temperatures between 0° and 20° is

$$\sigma = 0.9982 + 0.0000045(t-40)^2 + 0.0000005(20-t)^3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

and for temperatures between 20° and 60° the last term is omitted.

If equation (l) is multiplied by $d\theta$ and integrated between the limits θ_1 and θ_2, we have

$$\int_{\theta_1}^{\theta_2} \sigma \, d\theta = 0.9982\,(\theta_2 - \theta_1) + 0.0000045 \left\{ \frac{1}{3}(t_2 - 40)^3 - \frac{1}{3}(t_1 - 40)^3 \right\}$$

$$+ 0.0000005 \left\{ \frac{1}{4}(20 - t_1)^4 - \frac{1}{4}(20 - t_2)^4 \right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots (m)$$

Equation (m), substituted in equation (k), gives the complete expression which is to take the place of $-(H_2-H_1)$.

The value of h_0 for NaCL at concentration 400 is 448.2, and for concentration 200 the value of h_1 is 892.2. The difference between these numbers is 444, which, according to the theory proposed, is constant for all temperatures. The value of the second term in the right side of equation (k) varies with the temperature. Let θ_1 and t_1 equal 4° C. and θ_2 and t_2 equal 10° C.; then the last term in equation (k) becomes 451.9. The difference between 451.9 and 444 is 7.9, which is the value of the right side of equation (k). The corresponding value of $\frac{L_2 - L_1}{\theta_2 - \theta_1}$ the left side of equation (k), is found by experiment to be 8.5. In a similar manner for temperatures 10° to 20° the right side is 6.5 and the experimental value is 7.0. For temperatures 20° to 30° the right side is 5.66 and the experimental value is 5.7. The difference between 7.9 and 5.66 is 2.2, which is the change in the left side of equation (k) between 0° and 30°. This change will be the same for all solutions at concentration 200. While it is slightly too small for the NaCl, it is about right for KCl and KOH. At concentrations 100 this difference would be doubled, or 4.4. At 50 it would be 8.8, and at 25 it would be 17.6. With the exception of KNO_3, which has a very large variation, these last numbers are too large. As the solution becomes more dilute it is highly probable that the specific heat of the solution changes similarly to water, which would tend to reduce

[4] *Phil. Trans.* R. S. (1902), clxix, 142.

PLATE 1.

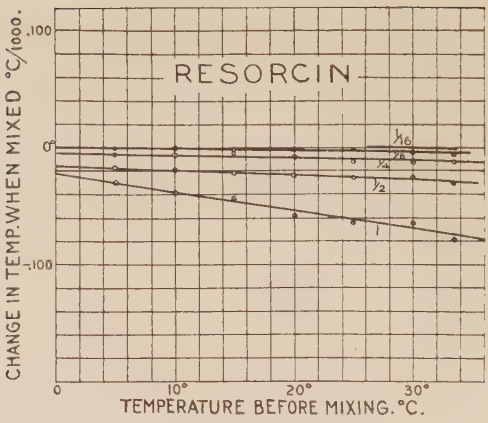
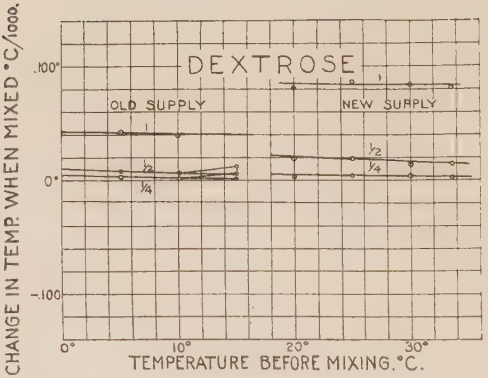


PLATE 2.



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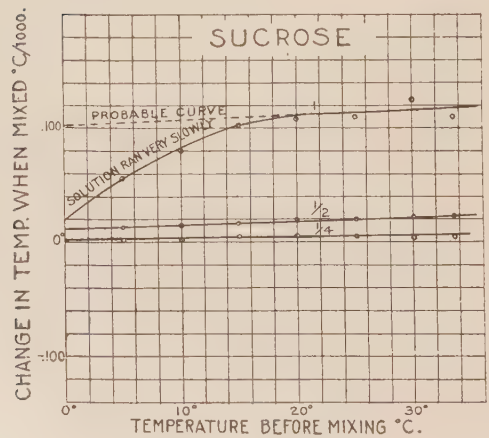

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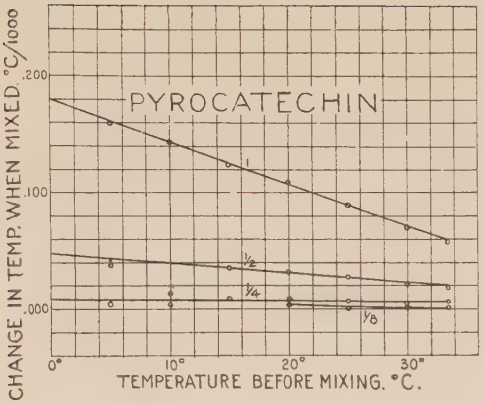

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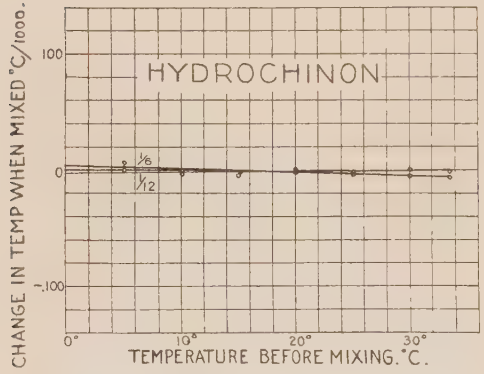

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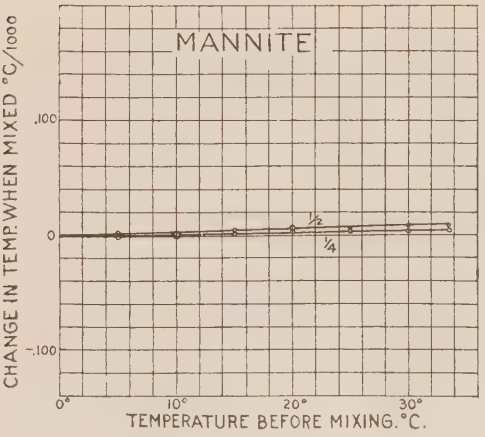

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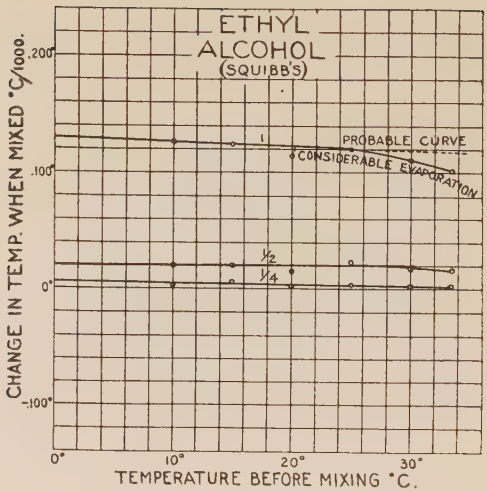

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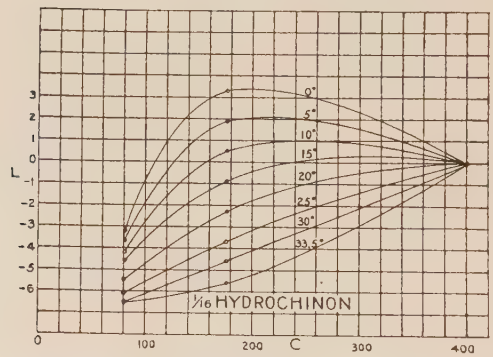

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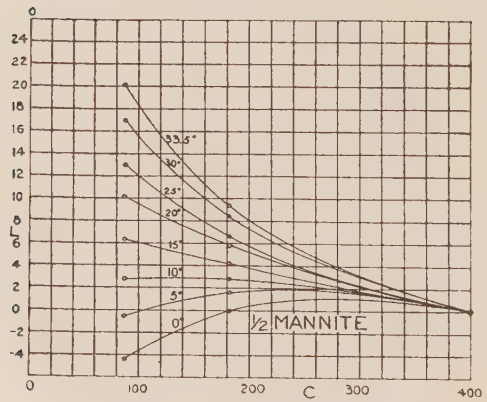


PLATE 10.

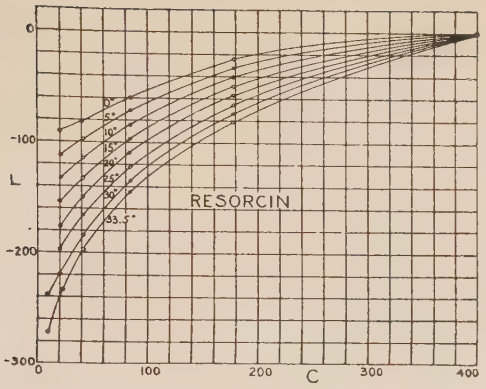


PLATE 11.

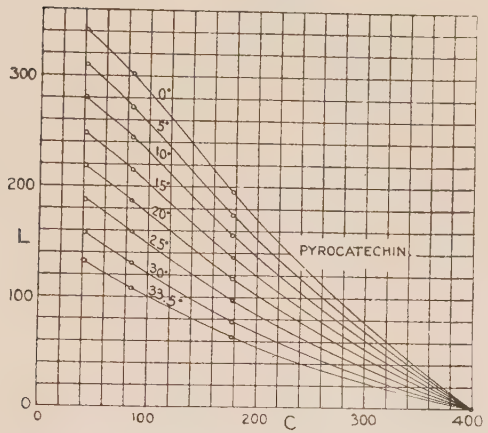


PLATE 12.

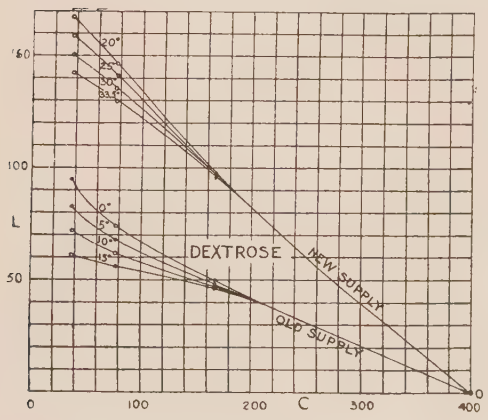


PLATE 13.

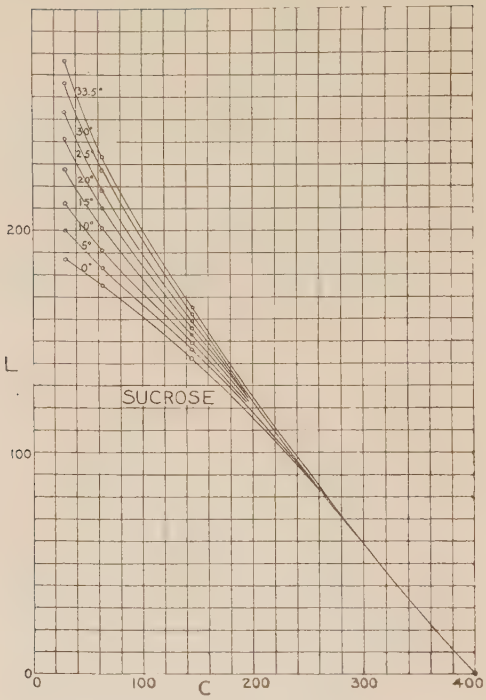
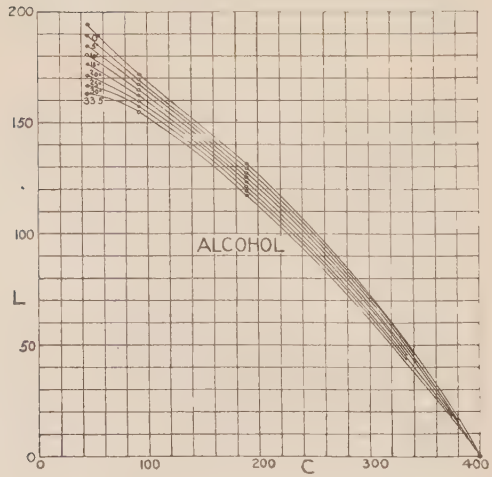


PLATE 14.



these numbers at the more dilute concentrations. When the change in the specific heats with respect to temperature for all concentrations of the several solutions is definitely known it may be possible to account for all the exceptions found in these results.

11. *Heats of Dilution of Non-electrolytes.*—The point of interest with the non-electrolytes is that the H is constant for all concentrations. Equation (a) equals zero, since $\frac{dH}{dm} = a = 0$, therefore $\frac{dl}{\theta d} = 0$ and $l = c$, a constant, and should not vary with the temperature. The (L, C) curves should be parallel and the curves in Plates 1 to 7 should be horizontal straight lines. The curves in Plates 1 to 7 are straight lines, but none of them is exactly horizontal. Resorcin and pyrocatechin show considerable variation from the horizontal, and this produces the fan-shaped (L, C) curves. If the (L, C) curves of the non-electrolytes were plotted to the same scale as the (L, C) curves of the electrolytes the lines would be very much closer together. The use of the much larger scale with several of the non-electrolytes exaggerates the small departure from the theory. It is of interest to note that, while the majority of the lines in Plates 1 to 7 slant slightly downward toward the right, there are two or three that slant upward toward the right. This proves conclusively that this slight variation was not due to any fault of the apparatus.

I take this opportunity to thank Prof. W. F. Magie for placing a room and the equipment of the Palmer Physical Laboratory at my disposal. I wish to express my appreciation of his kindly assistance and to acknowledge the many suggestions received from him and Prof. H. L. Cooke while carrying on the work.

PALMER PHYSICAL LABORATORY,
Princeton University,
June, 1917.

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